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THE ANALYSIS OF SULPHUR FORMS IN COAL

By

ALFRED R. POWELL

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THE ANALYSIS OF SULPHUR FORMS IN COAL.

By Alfred R. Powell.

INTRODUCTION.

Methods for the analysis of total sulphur in coal have been in use for many years and at the present time are so numerous that it would be folly to attempt to describe all of them. All depend on the general principle of complete oxidation of the coal, followed by estimation of the sulphates produced by this process. From a technical standpoint a total sulphur determination is useful as indicating one of the factors which fix the value of particular coals for use under steam boilers, for general heating, and for the manufacture of coke and gas.

For certain purposes, however, it is desirable to know not only the total sulphur content, but also how the sulphur is combined in the coal and the exact amount of each form present. Data of this kind would be useful in indicating how much of the sulphur-containing material can be removed from the coal by washing processes, what effect the sulphur has on the heating value of the coal, how the various sulphur forms behave during the coking and gas-making processes, and other facts of interest to coal technologists.

The main purpose of this investigation, undertaken by the Bureau of Mines, however, was to try out further the method of Powell and Parr for the analysis of sulphur forms in coal (described on p. 5), to determine its applicability to a variety of coals, and to introduce, if necessary, certain refinements of analysis. Preceding experiments had been chiefly with Illinois coals, so it was important to ascertain just how the method would apply to coals from other districts.

ACKNOWLEDGMENTS.

The author wishes to express his appreciation to A. C. Fieldner, under whose direction this investigation was conducted, for many valuable suggestions; to Prof. S. W. Parr for his constant interest in the coal sulphur problem and his advice and direction during the earlier stages of the work at the University of Illinois; and

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to E. A. Holbrook, who was the pioneer in stressing the importance of the problem of coal sulphur in its economic relation to the Nation.

HISTORICAL REVIEW.

Iron pyrites has been known as one of the constituents of coal for a great many years and investigators have had fairly good evidence that sulphur in organic combination also existed in coal. The first method proposed for the analysis of these two forms utilized sodium hypobromite.[2] The supposition was that the hypobromite dissolved the pyrites and sulphates without affecting the organic sulphur, but no proof was advanced to show that this was correct.

The action of bromine on coal sulphur was investigated and the conclusion reached that there was no selective solution of pyrites, but that some of the organic sulphur was taken into solution.[3] This was shown by variations in the iron-sulphur ratio of the extract from that corresponding to FeS_2.

A method depending on certain assumptions regarding coal sulphur has been used in recent years. The total iron in the coal minus any water soluble iron that may be present is considered to be iron combined as pyrites. From this is calculated the sulphur existing as pyrites. Any sulphur present as sulphate may be determined by a simple extraction with dilute acid; then the pyritic sulphur plus the sulphate sulphur when subtracted from the total sulphur gives the sulphur organically combined, provided no other form of sulphur exists in the coal. This method is faulty in that it disregards the presence of iron silicate and that the whole procedure is based on unproven assumptions regarding combinations of sulphur in the coal.

A method somewhat more satisfactory than the foregoing was devised by the Bureau of Mines in 1914, the work being done under the direction of A. C. Fieldner and F. D. Osgood. A large number of analyses were subsequently run on coals from various parts of the country in order to get an idea as to the organic sulphur content of coals from different districts.

In this process the coal is crushed to pass a 10-mesh screen and then sifted over a 60-mesh screen. The fine material is discarded and that remaining on the 60-mesh screen used for the analysis. This material is treated with a zinc chloride solution of 1.35 specific gravity, so that the heavy ash-containing material could sink. The coal substance remaining at the top of the solution contains only a few tenths of 1 per cent of iron, the remainder being carried down in the ash. This lighter fraction of the coal is then washed with dilute

[2] Drown, T. M., The determination of sulphur in sulphides and in coal and coke: Chem. News, vol. 43, 1881, p. 89.

[3] Fischer, Ferd., Ueber Lagerungsverluste und Selbstentzundung von Steinkohlen: Ztschr. angew. Chem., Bd. 12, 1899, p. 764.

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acid to remove sulphates or soluble iron compounds and the iron considered to be combined as pyrites. From this the sulphur combined as pyrites can be figured and the difference between it and the total sulphur in the coal fraction is taken as the organic sulphur.

This method is only fairly accurate for several reasons. To begin with, discarding the 60-mesh coal gives an unrepresentative sample. A small part of the organic sulphur might be carried down with the heavy fraction and the iron remaining in the lighter fraction might not be entirely combined as pyrites, since some of it may be present as iron silicate, for example. Furthermore, proof is lacking at this time that the sulphur assumed to be organic is actually so combined. Later experiments have proved, however, that this method is fairly accurate for organic sulphur, and the data thus obtained show that organic sulphur is present in most coal to a much greater extent than generally supposed.

POWELL AND PARR METHOD.

An accurate analytical method for the systematic analysis of sulphur forms in coal has been developed within recent years by A. R. Powell and S. W. Parr.[4] This may be described briefly as follows: Five-gram samples of the finely divided coal are taken for the sulphate analysis. These are extracted with 3 per cent hydrochloric acid at 60° C. for a period of 40 hours. The extract is analyzed for iron and sulphur, the sulphur representing the sulphate sulphur present in the coal.

For the pyrite analysis 1-gram samples are extracted with 80 c. c. portions of dilute nitric acid, specific gravity 1.12, for a period of 24 hours at room temperature. The extract is evaporated to dryness, taken up in hydrochloric acid, and analyzed for iron and sulphur. This sulphur represents the sulphur as pyrites plus the sulphur as sulphate. The latter form has already been determined, so by subtraction the pyritic sulphur content of the coal is given. This amount may then be checked to prove that it is the pyrite sulphur by the following calculation: The hydrochloric acid soluble iron is subtracted from the nitric acid soluble iron, thereby giving the iron combined as pyrites. By a simple stoichiometrical calculation the sulphur combined with the iron is obtained, and this should agree with the sulphur previously determined as pyritic sulphur. In the case of every coal tried these two figures checked, showing that the method is accurate for the pyritic sulphur.

That the remainder of the coal sulphur is organic is proved as follows: Phenol will extract a large quantity of material from coal,

[4] Powell, A. R., and Parr, S. W., A study of the forms in which sulphur occurs in coal: Bull. 111, Eng. Exp. Station, University of Illinois, 1919, pp. 10–35.

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this extracted substance having a great influence on coking quality.[5] The phenol soluble material is ashless and, therefore, organic. A portion of the coal sulphur is found in this extract, but not enough to account for all of the organic sulphur.

After the coal has been extracted with phenol the residue is treated with dilute nitric acid to remove the inorganic sulphur. After nitric acid treatment the coal forms a dark colloidal solution with ammonia, which may be filtered, leaving on the filter most of the ash and inorganic matter of the coal. The colloidal material of the filtrate is very low in ash, showing that inorganic substances are practically absent. This material is found to contain the remainder of the coal sulphur, which must be in an organic form, since it occurs in an organic fraction of the coal.

This method of analysis not only determines the inorganic sulphur forms directly, but also gives a method of proving that the remainder of the sulphur is organic—the first absolute proof that organic sulphur exists in coal in comparatively large quantities.

DESCRIPTION OF COALS USED IN EXPERIMENTS.

The coals analyzed by Powell and Parr were gathered principally from Illinois fields. It was decided, therefore, to run similar analyses of coals from other fields in order to determine the applicability of this method to coals of other districts. A small number of coals only was selected for these experiments, since the detailed study required considerable time for analyzing each coal. Furthermore, it was preferable to get samples which had stood some time so that there would be an appreciable amount of sulphate present, as in freshly mined coal this form of sulphur is usually very small in quantity. The following table gives a detailed description of each coal used:

TABLE 1.—*Source of coals used in experiments.*

Laboratory number of sample.	State.	County.	Post office.	Mine and bed.	Company operating mine.
23066	Pennsylvania	Butler	Chicora	Chicora, Upper Freeport.	Cunningham Coal Co.
18847	do	Allegheny	Bruceton	Experimental, Pittsburgh.	United States Bureau of Mines.
20507	West Virginia	McDowell	Switchback	Mine No. 7, Pocahontas No. 3.	Pocahontas Fuel Co.
21308	Kentucky	Letcher	Fleming	Mine No. 301, Elkhorn.	Elk Horn Coal Corporation.
21100	Tennessee	Morgan	Coalfield	Conger, Coal Creek.	Conger-Baker Co.
27224	Kansas	Cherokee	West Mineral.	Katy No. 9, Cherokee.	Mayer Coal Co.

[5] Parr, S. W., and Hadley, H. F., The analysis of coal with phenol as a solvent: Bull. 76, Eng. Exp. Station, University of Illinois, 1914.

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TABLE 2.—*Proximate analyses and calorific values of coals used in experiments.*[1]

Laboratory number of sample.	Proximate analysis.					Calorific value.	
	Moisture.	Volatile matter.	Fixed carbon.	Ash.	Sulphur.	Calories.	B. t. u.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*		
23066.....	2.04	33.11	56.36	8.49	1.21	7,450	13,410
18847.....	1.57	38.72	54.95	4.75	1.72	7,901	14,222
20507.....	.39	22.88	70.47	6.25	.56	8,133	14,639
21308.....	1.65	37.78	56.57	3.98	.71	7,910	14,238
21100.....	.74	39.05	52.40	7.80	4.25	7,821	14,078
27224.....	1.73	34.90	55.14	8.23	3.06	7,559	13,606

[1] All samples were in an air-dry condition.

METHODS USED IN EXPERIMENTS.

TOTAL SULPHUR.

Total sulphur determinations were made on each coal by the sodium peroxide method as used by Powell and Parr.[6] The results obtained by this method were very irregular, and investigation revealed that blank determinations on the sodium peroxide showed large quantities of sulphur which were not constant in amount for different portions of the same batch. Furthermore, the nickel crucibles were attacked by the hot, alkaline fusion to such an extent that some nickel was occluded by the barium sulphate in the final precipitation.

These difficulties led to the adoption of the Eschka method for determining sulphur in coal, and this was used not only in the determination of total sulphur but also for the sulphur in coal residues, throughout the investigation. The percentage of total sulphur in the coal as well as the percentage of the different sulphur forms is all figured on the basis of the air-dried coal.

SULPHUR AS SULPHATE.

The analysis for the sulphate content was performed by the method used by Powell and Parr. Five-gram samples of the coal were extracted with 300 cubic centimeters of 3 per cent hydrochloric acid for 40 hours. The beakers in which the extraction took place were kept over a water bath so as to be maintained at a temperature of about 60° C. The contents were then filtered and the filtrate analyzed for iron and sulphur. The Zimmermann-Reinhardt potassium permanganate titration method was used to determine the iron, and the sulphur was determined by the usual barium sulphate precipitation.

[6] Powell, A. R., and Parr, S. W., Work cited, pp. 10–35.

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SULPHUR AS PYRITES.

For the pyrite analysis 1-gram samples of the coal were allowed to stand with 80 c. c. portions of dilute nitric acid, specific gravity 1.12, for two or three days at room temperature. Twenty-four hours is probably sufficient for this extraction, but a longer time does no harm. If a shaking machine is available, the extraction time may be cut down materially.

The extract was then filtered off and the nitric acid evaporated on the water bath. The residue from this evaporation was taken up in hydrochloric acid and the resulting solution analyzed for iron and sulphur by the methods described above.

The iron obtained in the nitric acid extract represented that extracted by the hydrochloric acid plus the iron combined as pyrites; therefore the pyritic iron could be figured by the difference between the two iron determinations. The sulphur in the nitric acid extract represented the sulphate sulphur, which had been determined previously by hydrochloric acid treatment, plus the sulphur combined as pyrites. Moreover, if the dilute nitric acid were taking into solution any of the organic sulphur, it would have appeared in this extract. The question as to whether any of the organic sulphur was being taken into solution by the nitric acid could be answered by comparing the percentage of pyritic iron with what was presumably the percentage of pyritic sulphur. This latter was obtained by subtracting the percentage of sulphur as found in the hydrochloric acid extract from that in the nitric acid extract. If the pyritic iron and the sulphur were in the exact proportions to form FeS_2, the nitric acid was a selective solvent for pyrites in that particular coal. If the sulphur were in excess, however, the indications would be that the organic sulphur of that coal was being attacked by the dilute nitric acid. It was by these calculations that the accuracy of the method for pyritic sulphur was checked.

SULPHUR IN ORGANIC COMBINATION.

The amount of sulphur in organic combination was determined by much the same means used by Powell and Parr in their previous investigation. The phenol soluble type of organic sulphur was calculated from the difference between the total sulphur content of the coal and the sulphur content of the coal residue after phenol extraction.

The extraction of the coal by phenol was carried on in an oven, having a constant temperature of 150° C. Air condensers were so arranged that the vaporized phenol would be carried back into the extraction flasks. One-half-gram samples of coal and 25 c. c. of phenol were placed in the flasks, and the extraction allowed to pro-

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ceed for 20 hours. The contents were then filtered through a porcelain Gooch crucible and thoroughly rinsed with alcohol and ether. The entire asbestos mat, with its covering of coal residue, was ground up with the Eschka mixture, and the sulphur determination run in the usual manner. As stated before, the phenol soluble organic sulphur was obtained by difference. The phenol soluble material was known to be organic because of its lack of ash.

The so-called "humus" type of organic sulphur—that very stable portion which is not extracted by phenol—was determined directly by a method differing slightly from that of Powell and Parr. The residues from the dilute nitric acid extraction, previously described, were used for these studies, since all of the inorganic sulphur had been removed, and all of the organic sulphur of the coal was present, unless the dilute nitric acid had extracted a little of the organic sulphur. This last possibility would have been determined at the time of the nitric acid extraction; thus it can be safely said that all of the organic sulphur was present in the nitric acid residue or had been accounted for otherwise. In most cases, particularly where only a small amount is present, the phenol soluble sulphur will respond to the same treatment given the more stable humus organic sulphur; therefore the following method was used for the total organic sulphur determination. In the case of only one coal, where the phenol soluble sulphur was high, was it necessary first to extract with phenol, then with dilute nitric acid, to remove the inorganic sulphur, and then to finish the analysis for the humus type of organic sulphur by itself.

It was found that the residue from the dilute nitric acid extraction did not go into solution in the ammonia readily, hence this residue was treated further with concentrated nitric acid. The nitric acid was then evaporated off on the water bath, leaving the residue in such a condition that it dissolved easily in ammonia. For a semibituminous coal from the Pocahontas field, three treatments with nitric acid, followed each time by evaporation on the water bath, were necessary to digest the coal sufficiently for the alkaline solution.

The residues were then treated with 25 c. c. of concentrated aqua ammonia and allowed to stand for some time. They were then filtered through an ordinary paper filter, the filtration requiring about one week on account of the colloidal nature of the solution. Previous research had shown that this alkaline soluble material was almost ash free and therefore organic in nature. Most of the ash of the coal was left on the filter.

The dark brown, colloidal solution was evaporated to dryness on the water bath and the sulphur in the residue determined by the

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Eschka method. This, then, gave the total organic sulphur content of the coal by a direct procedure, unless the coal had been extracted previously with phenol, in which case the above process gave the humus type of organic sulphur by itself.

The above procedure showed whether or not the methods of analysis for the various forms of sulphur in the coal were accurate, and the only question remaining was as to the possible existence of any other form of sulphur in the particular coal studied. This was easily determined by adding together the percentages of the forms of sulphur for which analyses had been run and observing how this checked with the total sulphur of the coal as determined.

RESULTS OF THE EXPERIMENTS.

DIRECT DETERMINATION OF SULPHATE AND PYRITES SULPHUR AND OF ORGANIC SULPHUR BY DIFFERENCE.

The first set of experiments was performed with regard to the analysis of the sulphate and pyritic forms of the sulphur alone, a detailed study of the organic sulphur being postponed until later. The data from these experiments are given in the following tables:

Sulphur and iron in coal No. 23066, Upper Freeport bed, Chicora, Pa.

Constituents.	Per cent.	Per cent.
Total sulphur, as determined	1.21	
Sulphur soluble in dilute nitric acid	.54	
Sulphur soluble in dilute hydrochloric acid	.07	
Pyritic sulphur, by direct extraction		0.47
Iron soluble in dilute nitric acid	.52	
Iron soluble in dilute hydrochloric acid	.14	
Pyritic iron, by direct extraction	.38	
Pyritic sulphur, calculated from iron		.44
Difference of pyritic sulphur value from calculation		+.03

The check on the method for pyritic sulphur in this coal is fairly close, although a very small quantity of organic sulphur may have been taken into solution.

Sulphur and iron in coal No. 18847, Experimental mine, Bruceton, Pa.

Constituents.	Per cent.	Per cent.
Total sulphur, as determined	1.72	
Sulphur soluble in dilute nitric acid	1.02	
Sulphur soluble in dilute hydrochloric acid	.23	
Pyritic sulphur, by direct extraction		0.79
Iron soluble in dilute nitric acid	1.05	
Iron soluble in dilute hydrochloric acid	.37	
Pyritic iron, by direct extraction	.68	
Pyritic sulphur, calculated from iron		.78
Difference of pyritic sulphur value from calculation		+.01

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Sulphur and iron in coal No. 20507, mine No. 7, Switchback, W. Va.

Constituents.	Per cent.	Per cent.
Total sulphur, as determined	0.56	
Sulphur soluble in dilute nitric acid	.09	
Sulphur soluble in dilute hydrochloric acid	.01	
Pyritic sulphur, by direct extraction	.....	0.08
Iron soluble in dilute nitric acid	.43	
Iron soluble in dilute hydrochloric acid	.35	
Pyritic iron, by direct extraction	.08	
Pyritic sulphur, calculated from iron	.....	.09
Difference of pyritic sulphur value from calculation	.....	−.01

Sulphur and iron in coal No. 21308, Mine 301, Fleming, Ky.

Constituents.	Per cent.	Per cent.
Total sulphur, as determined	0.71	
Sulphur soluble in dilute nitric acid	.17	
Sulphur soluble in dilute hydrochloric acid	.04	
Pyritic sulphur, by direct extraction	.....	0.13
Iron soluble in dilute nitric acid	.32	
Iron soluble in dilute hydrochloric acid	.20	
Pyritic iron, by direct extraction	.12	
Pyritic sulphur, calculated from iron	.....	.14
Difference of pyritic sulphur value from calculation	.....	−.01

Sulphur and iron in coal No. 21100, Conger mine, Coalfield, Tenn. (first run).

Constituents.	Per cent.	Per cent.
Total sulphur, as determined	4.25	
Sulphur soluble in dilute nitric acid	2.64	
Sulphur soluble in dilute hydrochloric acid	.71	
Pyritic sulphur, by direct extraction	.....	1.93
Iron soluble in dilute nitric acid	2.49	
Iron soluble in dilute hydrochloric acid	.94	
Pyritic iron, by direct extraction	1.55	
Pyritic sulphur, calculated from iron	.....	1.77
Difference of pyritic sulphur value from calculation	.....	+.16

These results seemed to indicate that the organic sulphur was being attacked to some extent by the dilute nitric acid. In order to avoid this, a run was made in which the time of extraction was carefully limited to 24 hours only. Despite this change in the procedure, similar results were obtained, showing that this particular coal contained a small quantity of organic sulphur, which was easily oxidized and taken into solution.

The form of coal sulphur which is most likely to react in this manner is that part of the organic sulphur soluble in phenol, since the phenol insoluble organic sulphur compounds are very stable; therefore, samples of the coal were first extracted with phenol, in order to dispose of these less stable organic sulphur compounds, and

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the residue extracted with dilute nitric acid as before. The results are given below:

Sulphur and iron in coal No. 21100, Conger mine, Coalfield, Tenn. (final run).

Constituents.	Per cent.	Per cent.
Total sulphur, as determined	4.25	
Sulphur soluble in dilute nitric acid	2.46	
Sulphur soluble in dilute hydrochloric acid	.71	
Pyritic sulphur, by direct extraction	.....	1.75
Iron soluble in dilute nitric acid	2.48	
Iron soluble in dilute hydrochloric acid	.94	
Pyritic iron, by direct extraction	1.54	
Pyritic sulphur, calculated from iron	.....	1.76
Difference of pyritic sulphur value from calculation	.....	—.01

This run showed that some of the organic sulphur had been taken into solution by the dilute nitric acid, demonstrating clearly the necessity for check determinations on the iron content of nitric acid extracts of coal.

Sulphur and iron in coal No. 27224, Mayer No. 9 mine, Carona, Kans.

Constituents.	Per cent.	Per cent.
Total sulphur, as determined	3.06	
Sulphur soluble in dilute nitric acid	2.31	
Sulphur soluble in dilute hydrochloric acid	.32	
Pyritic sulphur, by direct extraction	.....	1.99
Iron soluble in dilute nitric acid	2.25	
Iron soluble in dilute hydrochloric acid	.49	
Pyritic iron, by direct extraction	1.76	
Pyritic sulphur, calculated from iron	.....	2.01
Difference of pyritic sulphur value from calculation	.....	—.02

It will be noticed that the analytical results for pyritic sulphur in all six of the coals tested check to within a reasonable experimental error. The summarized results of these analyses for sulphur forms in the coals are given in the following table. It is to be noted that the organic sulphur values are obtained by difference, as they would be in actual laboratory practice.

TABLE 3.—*Summary of direct analyses for sulphur forms in coal.*[1]

Coal samples.		Total.	Pyritic.	Sulphate.	Organic.
Laboratory number.	Source (State).				
23066	Pennsylvania	1.21	0.47	0.07	0.67
18847	do	1.72	.79	.23	.70
20507	West Virginia	.56	.08	.01	.47
21308	Kentucky	.71	.13	.04	.54
21100	Tennessee	4.25	1.75	.71	1.79
27224	Kansas	3.06	1.99	.32	.75

[1] Values given in per cents, air-dry basis.

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Freshly mined coal seldom contains any appreciable amount of sulphates. The comparatively large percentages shown in the above coals are due to the fact that all had stood in the sample room for several years before the experiments were performed. Since this investigation endeavored to verify the method of analysis rather than to indicate the nature of any set of coals, this aging of the coals was a decided advantage, in that it gave an appreciable amount of the sulphate form.

DIRECT DETERMINATION OF ORGANIC SULPHUR FORMS.

It was now necessary to prove by actual experiment that the sulphur assumed to be organically combined was entirely in this form. The results on the phenol soluble type of organic sulphur were as follows:

Phenol soluble organic sulphur in coals.

Coal samples.		Per cent.
Laboratory number.	Source (State).	
23,066.....	Pennsylvania.....	0.12
18,847.....	.....do.....	.20
20,507.....	West Virginia.....	.02
21,308.....	Kentucky.....	.09
21,100.....	Tennessee.....	.77
27,224.....	Kansas.....	.32

The results for the other type of organic coal sulphur, the so-called humus organic sulphur, are given below. This is the sulphur existing in compounds insoluble in phenol, very stable, and taken into solution only by treatment with concentrated nitric acid, followed by extraction with strong aqua ammonia. Except in the case of the Tennessee coal, the figures below were obtained by subtracting the phenol soluble sulphur from the total organic sulphur. As mentioned previously, the Tennessee coal was first extracted with phenol; hence, the final ammonia soluble fraction contained only the humus type of organic sulphur, which was thus given directly.

"Humus" type of organic sulphur in coals.

Coal samples.		Per cent.
Laboratory number.	Source (State).	
23,066....	Pennsylvania.....	0.50
18,847....	.....do.....	.46
20,507....	West Virginia.....	.44
21,308....	Kentucky.....	.42
21,100....	Tennessee.....	1.01
27,224....	Kansas.....	.39

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SUMMARY OF ANALYTICAL RESULTS.

The following table gives in condensed form the results of the analyses for the various forms of sulphur and a comparison of the total of these with the total sulphur of the coal:

TABLE 4.—*Summary of all analyses for sulphur forms in coal.*

Sulphur forms.	Coal samples.					
	No. 23066 (Pa.).	No. 18847 (Pa.).	No. 20507 (W. Va.).	No. 21308 (Ky.).	No. 21100 (Tenn.).	No. 27224 (Kans.).
Pyritic sulphur	0.47	0.79	0.08	0.13	1.75	1.99
Sulphate sulphur	.07	.23	.01	.04	.71	.32
Humus organic sulphur	.50	.46	.44	.42	1.01	.39
Phenol soluble organic sulphur	.12	.20	.02	.09	.77	.32
Total	1.16	1.68	.55	.68	4.24	3.02
Total by direct analysis	1.21	1.72	.56	.71	4.25	3.06
Difference between totals	.05	.04	.01	.03	.01	.04

It is evident from this table that the sum of the several analyses checks very closely with the total sulphur content of each coal. There can be no doubt, therefore, but that all the sulphur of these coals has been accounted for in the four forms—namely, pyritic, sulphate, phenol soluble organic sulphur, and phenol insoluble organic or humus sulphur.

A graphic representation of the results of these experiments is given in figure 1. This shows the relative quantities of the various sulphur forms in the coals, a comparison with total sulphur, and a comparison of the pyritic sulphur as obtained with the pyritic sulphur as calculated from the pyritic iron.

METHODS FOR THE ANALYSIS OF SULPHUR FORMS IN COAL.

For laboratory practice the following methods are suggested for the analysis of the sulphur forms in coal. These methods are essentially those suggested earlier by Powell and Parr, but a few changes are introduced, which, it is hoped, will make the process better adapted to commercial laboratory routine.

Three methods of analysis are given. The first is to be used where only the sulphate, pyritic, and total organic sulphur are desired. The second is to be used where the two forms of organic sulphur are to be determined separately. The third is the method which has been followed in the present investigation—a complete, direct analysis of every sulphur form and a basic check on the method of analysis. This latter method would find use only where a coal from a new field was being studied.

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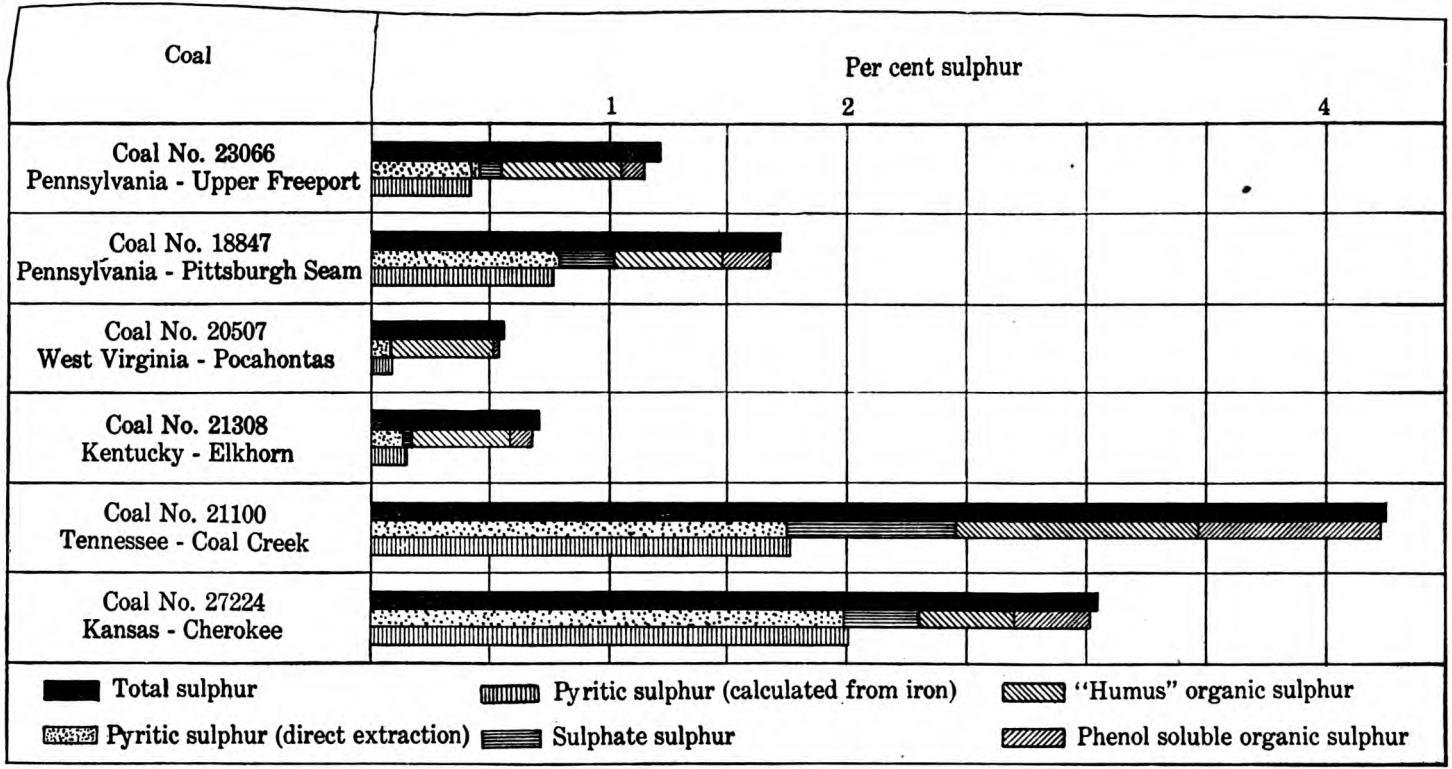

FIGURE 1.—Chart showing relative quantities of sulphur forms in a variety of coals, comparisons of the sum of these to total sulphur by the Eschka method, and comparison of the pyritic sulphur by two independent methods of analysis.

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A.—RAPID METHOD FOR SULPHATE, PYRITES, AND TOTAL ORGANIC SULPHUR.

Crush the air-dried coal so that it will pass completely through a 100-mesh screen. Weigh out a 5-gram sample and place it in a 500-c. c. beaker. Cover this carefully with 300 c. c. of 3 per cent hydrochloric acid, stir thoroughly, and place a watch glass on the beaker. Put this beaker on top of a water bath or some other warm place where it can digest at about 60° C.

At the end of 40 hours filter the contents of the beaker, discarding the coal material left on the filter. Add 2 c. c. of bromine water and heat almost to boiling. Pour this acid solution into an excess of ammonia and stir to coagulate the ferric hydroxide. Filter off this iron precipitate, retaining it for the iron determination later. Make the filtrate barely acid with hydrochloric acid, heat to boiling, and add slowly, with stirring, 10 c. c. of 10 per cent barium chloride. Allow this to stand for several hours, then filter it. Ignite the filter paper and weigh the precipitate of barium sulphate. The weight of barium sulphate, in grams, multiplied by 2.75, represents the percentage of sulphur, combined as sulphate, in the coal.

Dissolve the precipitate of ferric hydroxide off the filter with concentrated hydrochloric acid. Heat this acid solution to boiling and then add drop by drop, until colorless, a solution of stannous chloride (50 grams of stannous chloride and 100 c. c. of concentrated hydrochloric acid, diluted to 1 liter). Allow the solution to cool; then add 25 c. c. of a saturated solution of mercuric chloride, stirring thoroughly. Now dilute the contents of the beaker to 500 c. c. and add 20 c. c. of manganese sulphate solution (67 grams of crystallized manganous sulphate, 138 c. c. of phosphoric acid, specific gravity 1.7, and 130 c. c. of concentrated sulphuric acid, made up to 1 liter of solution). Titrate this solution with N/50 potassium permanganate to the faintest noticeable pink color. The number of cubic centimeters of N/50 potassium permanganate used, multiplied by 0.0223, gives the percentage of hydrochloric-acid soluble iron in the coal.

Now weigh out a 1-gram sample of the coal and place it in a 150 c. c. beaker. Cover it with 80 c. c. of dilute nitric acid (1 part of nitric acid, specific gravity 1.42, to 3 parts of water; specific gravity of mixture, 1.12). Allow this to stand for 24 hours, with occasional stirring, and filter. Discard the coal residue on the filter. Add 2 c. c. of concentrated hydrochloric acid to the filtrate and evaporate to dryness on the water bath. Dissolve the residue in 25 c. c. of water and 5 c. c. of concentrated hydrochloric acid. Pour this acid solution into an excess of hot, dilute ammonia. From this point the analysis is the same as that for the hydrochloric-acid soluble iron and sulphur. The weight of barium sulphate, in grams, multiplied by 13.75, rep-

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resents the percentage of sulphur, both pyritic and sulphate, in the coal. The number of cubic centimeters of N/50 potassium permanganate used multiplied by 0.1115 gives the percentage of iron, both pyritic and acid soluble, in the coal.

Figure the percentage of pyritic sulphur in the coal by subtracting from the percentage of sulphur obtained the percentage of sulphate sulphur. Also, as a check, subtract from the percentage of iron obtained the percentage of hydrochloric-acid soluble iron, multiply the result by 1.145, and note how it compares with the percentage of pyritic sulphur. If this calculated percentage is lower than that obtained directly, the calculated value should be considered the correct one. In fact, it would seem safe, for rapid analytical work, to calculate the pyritic sulphur from the iron in every case. This method of procedure would eliminate the sulphur determination on the nitric-acid extract, thereby saving considerable analytical work.

Commercial laboratories would probably find a saving of time for acid extractions if some type of shaking device were used. By this the time of extraction could probably be cut down to an hour for the nitric acid.

Calculate the total organic sulphur of the coal by adding the percentages of sulphate and pyritic sulphur and subtracting this from the per cent of total sulphur in the coal. The investigation has shown that this sulphur may safely be considered organic.

B.—METHOD FOR SULPHATE, PYRITES, AND TWO FORMS OF ORGANIC SULPHUR.

This method involves exactly the same procedure as method A, but another determination is added. Weigh 1 gram of the coal into a 50-c. c. Erlenmeyer flask. This should be fitted with a cork stopper, through which is inserted a straight glass tube about 2 feet long. Twenty-five c. c. of melted phenol is then poured into the flask, the stopper with the glass tube inserted, and the flask placed in an electric oven that maintains a temperature of 150° C. The glass tube should be so arranged that it protrudes from the oven into the room in order that it may act as a condenser for the phenol vapors.

At the end of 20 hours the flask is removed and the contents filtered, while hot, through a Gooch crucible. The residue is completely washed out of the flask into the crucible with alcohol and the washing with alcohol is continued until the alcohol runs through colorless. The residue is then washed with a small amount of ether and placed in an oven to dry. The residue, together with the asbestos mat, is completely removed from the crucible and ground in a mortar with

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twice its volume of Eschka mixture (1 part of sodium carbonate and 2 parts of calcined magnesia). This mixture is then placed in a porcelain crucible, covered with more of the Eschka mixture, and heated to a low red heat in a muffle or over a sulphur-free flame. After complete combustion of the coal residue the contents of the crucible are dissolved in hydrochloric acid, to which a little bromine water has been added. This solution is filtered and made alkaline with ammonia, then acidified slightly with hydrochloric acid. The sulphur is precipitated and determined as in method A. After the blank due to the Eschka mixture is subtracted the weight of barium sulphate, in grams, multiplied by 13.75 represents the percentage of sulphur insoluble in phenol. The percentage of phenol soluble organic sulphur is calculated by subtracting this from the per cent of total sulphur. The percentage of humus organic sulphur is calculated by subtracting the phenol soluble sulphur from the total organic sulphur.

C.—DETAILED METHOD FOR DIRECT DETERMINATION AND STUDY OF ALL SULPHUR FORMS IN COAL.

This involves the same procedure used in method B, but an extra determination is required. It is a direct estimation of the total organic sulphur, which in the other methods was found by difference. Take the residue from the dilute nitric acid extraction, including the filter paper, and place it in a small beaker. Cover this with concentrated nitric acid and place on a water bath to digest, leaving it there until the nitric acid has entirely evaporated. In the case of coals tending toward the semibituminous character, the treatment should be repeated several times.

Pour over the dry residue 25 c. c. of concentrated ammonia and stir thoroughly. Dilute somewhat and filter the solution through an ordinary filter paper. This filtration will probably require several days. Evaporate the dark brown filtrate to dryness on the water bath and remove the residue with a spatula. Grind this with the Eschka mixture, as described under method B, and determine the sulphur in the same manner. After substracting the blank due to the Eschka mixture, the weight of barium sulphate, in grams, multiplied by 13.75, represents the percentage of total organic sulphur in the coal. If the coal is normal, this percentage should check fairly close to the percentage of total organic sulphur obtained by difference.

CONCLUSIONS.

1. The method of Powell and Parr gives correct and accurate results for the analysis of sulphur forms in coal, as proved by experiments on a variety of coals from different fields. Detailed laboratory procedure methods are given in this paper.

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2. Dilute nitric acid will extract small amounts of organic sulphur from certain coals. The organic sulphur extracted is the unstable phenol soluble form. In order to avoid this error in laboratory determinations, it is recommended that the pyritic sulphur be calculated from the pyritic iron value.

3. The acid extractions of the coal can probably be materially shortened by using a shaking machine.

4. The dilute nitric acid not only extracts the pyrites quantitatively but also the same iron and sulphur taken into solution by dilute hydrochloric acid. For this reason samples intended for dilute nitric-acid extraction do not need to be extracted first with hydrochloric acid.

5. Semibituminous coals and the harder varieties of bituminous coals must be digested for a long time with concentrated nitric acid before the organic matter will become completely soluble in ammonia.

6. The Eschka method is preferable to the sodium peroxide method for the analysis of the sulphur in the coal and the coal residues unless the sodium peroxide used has a low and constant sulphur content.

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